PATENT SPECIFICATION

NO DRAWINGS **828,381**

Date of Application and filing Complete Specification: Oct. 15, 1957.

No. 32110/57.

Application made in United States of America on Oct. 18, 1956.

Complete Specification Published: Feb. 17, 1960.

ERRATA

SPECIFICATION NO. 828,381

Page 3 Table 1 heading *for* "Three-layered Control With 15-Mill" *read* "Three-layered Control With 15-Mil"

Page 5 line 61 *after* "layers" *insert* "are"

THE PATENT OFFICE,
6th April, 1960

DS 73933/1(18)/3945 200 3/60 DL

performed, to be particularly described in and by the following statement:—

This invention relates to safety-glass laminates.

The customary safety glass, which finds its principal use as a glazing for vehicles, is a laminate of two sheets of plate glass with an interlayer of polyvinyl butyral resin. The glass layers are usually about one-eighth inch in thickness, while the resin interlayer is usually 15 mils (0.015 inch) in thickness. Because of increased operating speeds of modern vehicles and the increased amount of traffic, there is an ever increasing danger that the customary safety glass will be ruptured when the force of a vehicular collision throws an occupant of the vehicle against the safety glass. Although splinters and broken pieces of glass are effectively prevented from scattering when the customary safety glass is broken, the head, or other member of the body, of a person thrown against the safety glass may penetrate the glass structure; in which event, jagged fragments of glass adhering to the resin interlayer may, and frequently do, according to studies made of automobile crashes, cause fatal or serious injury to that person. It is, of course, necessary in strengthening the safety-glass structure to provide some resiliency rather than hardness so that, if the skull hits the safety glass, it is decelerated without causing a concussion.

It has now been found that a sheet of biaxially oriented polyethylene terephthalate when included in a safety-glass laminate provides a resilient, energy-absorbing layer which

ponent layers, consisting of a ... of biaxially oriented polyethylene terephthalate, a layer of plasticized polyvinyl butyral, on each side of said polyethylene terephthalate, and a sheet of glass bonded to the outer surface of each layer of said polyvinyl butyral. The thicknesses of the layers are chosen according to the properties which the safety-glass is desired to have. For example, the polyethylene terephthalate may be very thin (0.5 mil) or thick (10 mils or more) depending upon the desired increase in rupture strength, although when the safety glass is to be used in automotive vehicles, from 1 to 5 mils represents the preferred range. In the same manner the layers of polyvinyl butyral resin and the panes of glass may be of various thicknesses, although, when the safety glass is to be used in automotive vehicles, the resin layers are preferably from 10 to 100 mils in thickness and the glass from one-sixteenth to one-quarter inch thick. For other applications, such as bullet-proof windows, industrial equipment uses, glass doors, glass construction panels, and display cases, the thicknesses of the various components of this laminate may be increased or decreased beyond the preferred ranges to suit the intended purposes.

It is rather difficult to obtain a good adhesive bond between polyethylene terephthalate and polyvinyl butyral. It is preferred, therefore, in order to ensure good adhesion, to subject the surface of the polyethylene terephthalate to direct contact with flame, preferably a gas flame, for a period of time sufficient to alter the surface characteristics of the treated

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Index at acceptance:—Class 140, A(2L: 2N3: 4).

International Classification:—C03c.

COMPLETE SPECIFICATION

Safety-Glass Laminates

We, E.I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, (Assignee of WILBERT LEE GORE, ALVA LEWIS HERMAN and STANLEY HIRAM MUNGER), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to safety-glass laminates.

The customary safety glass, which finds its principal use as a glazing for vehicles, is a laminate of two sheets of plate glass with an interlayer of polyvinyl butyral resin. The glass layers are usually about one-eighth inch in thickness, while the resin interlayer is usually 15 mils (0.015 inch) in thickness. Because of increased operating speeds of modern vehicles and the increased amount of traffic, there is an ever increasing danger that the customary safety glass will be ruptured when the force of a vehicular collision throws an occupant of the vehicle against the safety glass. Although splinters and broken pieces of glass are effectively prevented from scattering when the customary safety glass is broken, the head, or other member of the body, of a person thrown against the safety glass may penetrate the glass structure; in which event, jagged fragments of glass adhering to the resin interlayer may, and frequently do, according to studies made of automobile crashes, cause fatal or serious injury to that person. It is, of course, necessary in strengthening the safety-glass structure to provide some resiliency rather than hardness so that, if the skull hits the safety glass, it is decelerated without causing a concussion.

It has now been found that a sheet of biaxially oriented polyethylene terephthalate when included in a safety-glass laminate provides a resilient, energy-absorbing layer which increases the rupture strength of the safety glass.

According to one feature of the present invention, a safety-glass laminate consists of or includes a layer of plasticized polyvinyl butyral bonded on one side to a sheet of glass and on the other side to a sheet of biaxially oriented polyethylene terephthalate. According to a further feature of the invention there is provided a safety-glass laminate of five component layers, consisting of a central layer of biaxially oriented polyethylene terephthalate, a layer of plasticized polyvinyl butyral, on each side of said polyethylene terephthalate, and a sheet of glass bonded to the outer surface of each layer of said polyvinyl butyral. The thicknesses of the layers are chosen according to the properties which the safety-glass is desired to have. For example, the polyethylene terephthalate may be very thin (0.5 mil) or thick (10 mils or more) depending upon the desired increase in rupture strength, although when the safety glass is to be used in automotive vehicles, from 1 to 5 mils represents the preferred range. In the same manner the layers of polyvinyl butyral resin and the panes of glass may be of various thicknesses, although, when the safety glass is to be used in automotive vehicles, the resin layers are preferably from 10 to 100 mils in thickness and the glass from one-sixteenth to one-quarter inch thick. For other applications, such as bullet-proof windows, industrial equipment uses, glass doors, glass construction panels, and display cases, the thicknesses of the various components of this laminate may be increased or decreased beyond the preferred ranges to suit the intended purposes.

It is rather difficult to obtain a good adhesive bond between polyethylene terephthalate and polyvinyl butyral. It is preferred, therefore, in order to ensure good adhesion, to subject the surface of the polyethylene terephthalate to direct contact with flame, preferably a gas flame, for a period of time sufficient to alter the surface characteristics of the treated

material, but not for a period of time long enough to change the dimensional characteristics of the material. The general procedure and apparatus of the flame treatment process is that described with respect to polyethylene in United States Patents Nos. 2,648,097, 2,683,894, and 2,704,382, and British Patent No. 704,665. A useful variation of those processes is that wherein the sheet is subjected to the direct action of the flame two or more times, each of which times is shorter in duration than the time which would have been employed had the sheet been subjected only once to the flame.

There are other known procedures for treating the surfaces of polyethylene articles in order to make them printable or capable of being used with an adhesive, but most of these procedures do not seem to be operable with polyethylene terephthalate as will be illustrated in the succeeding examples. Moreover, other polymeric materials have been tried as a central layer between two plasticized polyvinyl butyral layers in a safety-glass laminate but none combines adequately the properties of optical clarity, ability to be bonded tightly to polyvinyl butyral, resiliency, and toughness.

The following examples illustrate how the invention may be performed.

EXAMPLE 1.

Several safety-glass laminations were made for comparison tests of their physical properties. The polyethylene terephthalate or other polymeric sheet employed in these tests was flame-treated on both sides prior to being incorporated in the laminate. The flame treatment was accomplished by mounting the polyethylene terephthalate on an internally cooled stainless steel rotatable drum, and passing the film, by rotating the drum, under a stationary row of gas burners. The gas supplied to the burner was a mixture of methane and air in a volumetric ratio of about 0.110 and 0.133. The burner was positioned 3/8 inch from the surface of the film and the linear speed with which the film was passed through the gas flame was 250 feet per minute.

The lamination was prepared by assembling the various components of the laminate and subjecting the laminate to a first pressing operation at 100 p.s.i. and 30°C. for .03 minutes, a second pressing operation at 100 p.s.i. and 60°C. for .03 minutes, and a third pressing operation at 100 p.s.i. and 90°C. for .03 minutes, following which, the laminate was placed in oil in an autoclave at 225 p.s.i. and 135°C. for 7 minutes. The physical properties of the laminates are tabulated below in Table 1. Two control laminates are shown, both having three layers (2 panes of glass and an interlayer of a 15-mil sheet or a 30-mil sheet of polyvinyl butyral). The other three specimens were laminates of five layers, two outside layers of glass, two intermediate layers of 15-mil polyvinyl butyral, and a central layer of 3-mil or 5-mil biaxially stretched flame-treated polyethylene terephthalate or untreated synthetic linear polyamide as indicated. The synthetic linear polyamide employed (Polyamide) was a polymer product of hexamethylenediamine and adipic acid.

TABLE I

Physical Test	Footnote	Three-layered Control With 15-Mill Interlayer of Polyvinyl Butyral	Three-layered Control With 30-Mil Interlayer of Polyvinyl Butyral	Five-layered Laminate With 5-Mil Central Layer of Polyethylene Terephthalate	Five-layered Laminate With 3-Mil Central Layer of Polyethylene Terephthalate	Five-layered Laminate With 3-Mil Central Layer of Polyamide
Adhesion	1	—	—	8—9 lbs.	12 lbs.	3—4 lbs.
−18° C. Break Height	2	3 ft.	5 ft.	24 ft.	18 ft.	—
+50° C. Break Height	2	8 ft.	13 ft.	Greater than 52 ft.	Greater than 52 ft.	—
Haze	3	Less than 0.3%	0.6%	2.0%	—	2.5%

Footnotes:

1. Results indicate the force in pounds necessary to peel one sheet of polyvinyl butyral from the film forming the central layer thus measuring the adhesion bond. Samples used in this test were 3 inches wide, and the stripping force was applied by a crosshead moving at a speed of 10 inches per minute.

2. Test used a general procedure of the Fracture Test No. 7 set forth in American Standards Association Test Specification Z 26.1—1950 with the single exception that a two-pound ball was used instead of a one-half-pound ball.

3. American Society for Testing Materials D1003—52.

EXAMPLE 2.

Laminates were prepared of five layers comprising two sheets of glass, two layers of 15-mil polyvinyl butyral, and one central layer of polyethylene terephthalate. The general lamination procedure was the same as that described in Example 1 except that methods other than flame treatment were used to treat both surfaces of the polyethylene terephthalate so as to enhance their adhesive qualities. The treatments involved dipping the polyethylene terephthalate film into the indicated liquids at the indicated temperature for a period of 30 seconds, followed by removing the film from the liquid and washing with distilled water and drying in an air oven for 3—5 minutes. The thus treated films were then laminated with sheets of polyvinyl butyral and glass sheets and tested for adhesion as described in Example 1. The test results are shown in Table 2. The adhesive properties of laminates made with 3-mil treated polyethylene terephthalate are compared with those of laminates made with untreated 1-mil polyethylene terephthalate. The results of many other experiments have shown that the thickness of the polyethylene terephthalate does not affect the test results of the laminate.

TABLE II

Treating Liquid	Concentration	Temperature of Treating Liquid	Adhesion of Laminate Containing Untreated 1-Mil Polyethylene Terephthalate**	Adhesion of Laminate Containing Treated 3-Mil Polyethylene Terephthalate**
Nitric Acid	Concentrated	80° C.	0.8 lbs.	3.5* lbs.
Aqua Regia	"	Room Temp.	1.0 "	1.1 "
Aqua Regia	"	70° C.	1.0 "	1.2 "
Potassium Permanganate	Saturated Solution at Room Temperature	Room Temp.	1.0 "	1.8 "
Potassium Permanganate	"	70° C.	1.0 "	2.0 "
Chromic Acid in Water	"	Room Temp.	0.9 "	4.0 "
Chromic Acid in Water	"	70° C.	0.9 "	6.0 "
Chromic Acid in Sulphuric Acid	"	Room Temp.	1.0 "	2.0 "
Chromic Acid in Sulphuric Acid	"	70° C.	0.9 "	5.0 "

* Polyethylene terephthalate film was distorted and shrunken by this treatment.

** Results indicate the force in pounds necessary to peel one sheet of polyvinyl butyral from the film forming the central layer, thus measuring the adhesion bond. Samples used in this test were 3 inches wide, and the stripping force was applied by a crosshead moving at a speed of 10 inches per minute.

These results indicate that a concentrated solution of chromic acid in water at 70°C. is the most successful agent for increasing the adhesion of the laminate.

EXAMPLE 3.

A laminate was prepared by forming a sandwich structure of a 15-mil sheet of plasticized polyvinyl butyral as the central layer, a 1/8 inch sheet of plate glass as one outside layer, and a 2-mil sheet of biaxially oriented polyethylene terephthalate as the other outside layer. The lamination was accomplished by the same general procedure as that described in Example 1 except that the polyethylene terephthalate was not subjected to a flame treatment in order to enhance its adhesion to the polyvinyl butyral. A control laminate was made identical to that just described except that the sheet of polyethylene terephthalate was omitted.

Break-height measurements were made by the procedure set forth in the 5.6 Impact, Test No. 6 (Ball Test, 10-Foot Drop) as modified by the 5.7 Fracture Test No. 7 described on page 15 of the publication of American Standards Association Incorporated No. Z 26.1—1950 entitled "American Standard Safety Code for Safety Glazing Materials for Glazing Motor Vehicles Operating on Land Highways." The measurements were made, however, at −18°C. In each case the test was run twice, once with the glass layer being struck with the falling ball ("glass-up"), and the other time with the opposite side of the laminate being struck with the falling ball ("glass down"). The results are shown in Table III.

TABLE III

Laminate with a layer of Polyethylene Terephthalate		Laminate without a layer of Polyethylene Terephthalate	
Glass up	21 feet	Glass up	17 feet
Glass down	46 feet	Glass down	24 feet

WHAT WE CLAIM IS:—

1. A safety-glass laminate consisting of or including a layer of plasticized polyvinyl butyral bonded on one side to a sheet of glass and on the other side to a sheet of biaxially oriented polyethylene terephthalate.

2. A safety-glass laminate of five component layers consisting of a central layer of biaxially oriented polyethylene terephthalate, a layer of plasticized polyvinyl butyral on each side of said polyethylene terephthalate, and a sheet of glass bonded to the outer surface of each layer of said polyvinyl butyral.

3. A safety-glass laminate as claimed in claim 2 in which the central layer of a biaxially oriented sheet of polyethylene terephthalate is from 1 to 5 mils in thickness.

4. A safety-glass laminate as claimed in claim 2 or 3 in which the polyvinyl butyral layers from 10 to 100 mils in thickness.

5. A safety-glass laminate as claimed in claim 2, 3 or 4 in which the sheets of glass are from one-sixteenth to one-quarter inch thick.

6. A safety-glass laminate as claimed in any of claims 1 to 5 in which the surface or surfaces of the sheet of polyethylene terephthalate contiguous to the layer or layers of plasticized polyvinyl butyral has or have been subjected to direct contact with a flame so as to enhance its or their ability to adhere to polyvinyl butyral.

7. A safety-glass laminate which includes a sheet of biaxially oriented polyethylene terephthalate, as herein particularly described and illustrated by the examples.

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